TECHNICAL MEMORANDUM

MOBILE TAGA SURVEY

AMBIENT PCB's

R.M.C., KINGSTON

FEBRUARY/MARCH 1986

ARB-114-86-AQM

OCTOBER, 1986

Ontario
Ministry of the Environment

E. PICHÉ, Director
Air Resources Branch

TECHNICAL MEMORANDUM

Mobile TAGA Survey
Ambient PCB's
R.M.C., Kingston
February/March 1986

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Prepared for
The Ontario Ministry of the Environment

Prepared by
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October, 1986

INS3/18

EXECUTIVE SUMMARY

On February 12, 20, 22 and March 12, 1986 the mobile TAGA unit of the Air Resources Branch conducted an air monitoring survey at the Royal Military College of Canada in Kingston, Ontario. The survey objective was to provide near real-time measurements of volatile PCB's during four (4) PCB destruction tests involving the mobile plasma arc unit operated by Pyrolysis Systems Incorporated.

In all, over 500 2-minute ambient air samples were collected and analysed, on-site, for selected volatile PCB's. All measurements for PCB's were below the analytical detection limits of 0.04 ug/m^3 for total (di to pentachlorobiphenyls) PCB's. Consequently, none of the 37 $\frac{1}{2}$-hour averaged concentrations for ambient PCB's exceeded the Ministry guideline of 0.45 ug/m^3.

INTRODUCTION

The mobile TAGA unit of the Air Resources Branch conducted an ambient air survey in Kingston, Ontario, during February and March, 1986. The survey objective was to monitor the ambient air for selected PCB congeners during the testing of the Pyroplasma mobile PCB destruction unit at the Royal Military College of Canada (RMC), Kingston.

The TAGA's primary purpose was to provide protection to the local residents against the possibility of elevated levels of airborne PCB's. The mobile TAGA technique affords near real-time detection of selected gaseous PCB's at the time of their potential release into the atmosphere. It is the only method currently available to the Ontario Ministry of the Environment by which the ambient air can be scanned for PCB's on-site, providing valuable air quality data necessary for immediately assessing the environmental impact of the PCB destruction process.

In all four (4) PCB destruction tests were conducted at RMC by Pyrolosis Systems Inc., one test per day on February 12, 20, 22 and March 12, 1986. The first test ran for approximately 2½ hours whereas the three latter tests ran for roughly 6 hours each. The TAGA acquired ambient air PCB concentration data during the testing periods. This report describes the TAGA PCB measuring technique, and summarizes the monitoring results obtained during the Kingston survey.

TAGA TECHNOLOGY AND SURVEY STRATEGY

A detailed description of the PCB monitoring technique is provided in Appendix A. Briefly, the TAGA (Model 3000) is a specialized single quadrupole

mass spectrometer with an atmospheric-pressure, chemical ionization (APCI) source. When monitoring PCB's, the TAGA ion source is coupled to an Automated Short Term Absorber (ASTA), which is simply a PCB preconcentrator and thermal desorption device.

The TAGA/ASTA technique provides ambient PCB measurements in 2 minute intervals. The ½-hour average concentrations are computed by averaging 15 consecutive 2-minute samples. In this study the PCB congeners targetted were the di-, tri-, tetra-, and pentachlorobiphenyl congeners.

The survey strategy was to position the mobile TAGA unit directly downwind of the plasma arc unit and acquire PCB measurements during the testing periods. All downwind sampling locations were between 100 and 300 metres from the potential source. Prior to the start of the PCB destruction tests the TAGA was calibrated for PCB detection and background data was acquired for a period of at least 30 minutes. The background data were used to correct the downwind measurements.

Calibrations of the TAGA/ASTA for gaseous PCB's were performed at least twice daily. Detection limits were typically 0.01 ug/m^3 per congener or 0.04 ug/m^3 for total (di to penta chlorobiphenyls) PCB's. The relative standard deviations for multiple injections of known PCB standards were generally better than 5% at the 0.425 ug/m^3 level.

During the tests, Mr. G. Wong of ARB's Emission Technology and Regulation Development Section provided the TAGA crew with pertinent information regarding the operational status of the destruction unit. Mr. M. Ladouceur of the Southeastern Region assisted the TAGA unit in the selection of the monitoring sites. The Southeastern Region was informed of the PCB monitoring results as they became available.

RESULTS AND DISCUSSION

In all, four (4) PCB destruction tests were conducted by Pyrolysis Systems Incorporated at the RMC test site. The data and time periods were approximately:

1) Test 1 February 12/86, 13:00-15:30 hours
2) Test 2 February 20/86, 10:30-16:30 hours
3) Test 3 February 22/86, 10:30-16:00 hours
4) Test 4 March 12/86, 15:00-21:00 hours

The mobile TAGA unit was present for all test burns acquiring ambient PCB concentration data on a continuous basis.

Accessability near the RMC test site was good, enabling the TAGA unit to select appropriate downwind locations for monitoring. Except for the low ambient temperatures, meteorological conditions were favourable for air monitoring. Wind speeds were generally low (less than 20 km/hr) and fairly consistent, allowing the TAGA unit to remain stationary for extended periods of time, as opposed to plume tracking. The meteorological data are reproduced in Appendix B. All monitoring sites were within the desired distance: between 100 and 300 metres from the source (see Figure 1). Note that the monitoring sites were in close proximity to the 24-hour air samplers set out by the Southeastern Region.

Including background samples a total of 545 2-minute air samples were screened for PCB's using the TAGA/ASTA technique. Downwind samples acquired during the test burns numbered 420 whereas 125 background samples were collected. Background samples were usually taken directly upwind of the test site. Occasionally, however, some background samples were acquired downwind of the test site prior to the addition of PCB's to the plasma arc.

The survey findings are summarized in Tables 1 to 4. The readings from fifteen (15) consecutive 2-minute samples were averaged to yield the ½-hour concentrations for total PCB's measured by the TAGA. None of the 37 ½-hour average concentrations for ambient gaseous PCB's exceeded the Ministry guideline of 0.45 ug/m^3. In fact, at no time were PCB's even detected above the analytical detection limits.

For this particular survey it was found that the PCB detection limits were uncommonly low - averaged 0.01 ug/m^3 per PCB congener. Lower than normal detection limits are attributed to the consistently low background levels of interferences (contaminants at same nominal molecular weight as the targetted PCB's). Since the ambient temperatures during the monitoring periods were often below 0°C, volatile organic loadings and subsequently the detection limits for PCB's were low. (In previous PCB surveys conducted in the warmer fall months the detection limits were five times higher or 0.05 ug/m^3 per congener.) The low ambient temperature may account for the non detection of PCB's. Note that the TAGA/ASTA technique measures gas phase PCB's, not those existing as aerosols or particulates. Therefore it is recommended that future PCB test burns requiring mobile TAGA monitoring be conducted during the warmer seasons.

TABLE 1

TAGA PCB SURVEY: KINGSTON RMC (PYROPLASMA)

February 12, 1986

Data Summary Test No. 1

Sample No.	Time Period	Site[1]	Met Conditions[2] AT	WD	WS	½-hour av.[3] (ug/m^3)	Comments
1-1	12:24-12:56	2	-7	WSW	5-10	ND	background
1-2	13:04-13:36	2	-7	WSW	10-15	ND	burning PCB's
1-3	13:42-14:14	2	-7	WSW	10-20	ND	burning PCB's
1-4	14:14-14:46	2	-6	WSW	5-15	ND	burning PCB's
1-5	15:01-15:33	2	-6	WNW	15-25	ND	Winds shifted north

1: See Figure 1 for sampling locations

2: AT = ambient temperature (^oC); WD = (predominant) wind direction; WS = wind speed range in km/hr

3: ½-hour concentration of gaseous PCB's (di- to pentachlorobiphenyls); mean of 15 2-minute samples; ND = not detected above detection limit of 0.04 ug/m^3

TABLE 2

TAGA PCB SURVEY: KINGSTON RMC (PYROPLASMA)

February 20, 1986

Data Summary Test No. 2

Sample No.	Time Period	Site[1]	Met Conditions[2] AT	WD	WS	½-hour av.[3] (ug/m^3)	Comments
2-1	09:52-10:24	3	3	ESE	0-3	ND	background
2-2	10:36-11:08	3	3	SE	0-3	ND	burning PCB's
2-3	11:08-11:40	3	4	SE	0-3	ND	burning PCB's
2-4	12:19-12:51	4	3	S	5-15	ND	burning PCB's
2-5	12:51-13:23	4	4	SSE	0-10	ND	winds shifted north
2-6	13:54-14:26	4	3	SSE	5-10	ND	flame out
2-7	14:26-14:58	4	4	S	0-10	ND	burning PCB's
2-8	15:01-15:33	4	4	S	0-10	ND	burning PCB's
2-9	15:33-16:05	4	4	S	3-10	ND	burning PCB's
2-10	16:05-16:37	4	4	S	0-10	ND	burning PCB's

1: See Figure 1 for sampling locations

2: AT = ambient temperature (^{o}C); WD = (predominant) wind direction; WS = wind speed range in km/hr

3: ½-hour concentration of gaseous PCB's (di- to pentachlorobiphenyls); mean of 15 2-minute samples; ND = not detected above detection limit of 0.04 ug/m^3

TABLE 3

TAGA PCB SURVEY: KINGSTON RMC (PYROPLASMA)

February 22, 1986

Data Summary Test No. 3

Sample No.	Time Period	Site[1]	Met Conditions[2] AT	WD	WS	½-hour av.[3] (ug/m^3)	Comments
3-1	10:29-11:01	5	-12	NE	5-25	ND	background (upwind)
3-2	11:38-12:10	6	-10	NNE	3-10	ND	PCB's (downwind)
3-3	12:10-12:42	6	-9	NNE	3-10	ND	PCB's (downwind)
3-4	12:42-13:14	6	-8	NE	5-25	ND	PCB's (downwind)
3-5	14:09-14:41	6	-7	NE	5-25	ND	PCB's (downwind)
3-6	14:54-15:26	6	-6	NE	5-15	ND	PCB's (downwind)
3-7	15:26-15:58	6	-6	NE	5-10	ND	MEK only, no PCB's

1: See Figure 1 for sampling locations

2: AT = ambient temperature (^{o}C); WD = (predominant) wind direction; WS = wind speed range in km/hr

3: ½-hour concentration of gaseous PCB's (di- to pentachlorobiphenyls); mean of 15 2-minute samples; ND = not detected above detection limit of 0.04 ug/m^3

TABLE 4

TAGA PCB SURVEY: KINGSTON RMC (PYROPLASMA)

March 12, 1986

Data Summary Test No. 4

Sample No.	Time Period	Site[1]	Met Conditions[2] AT	WD	WS	½-hour av.[3] (ug/m^3)	Comments
4-1	09:33-10:05	7	-1	NE	5-15	ND	background (upwind)
4-2	10:55-11:27	8	1	E	0-10	ND	background (downwind)
4-3	11:27-11:59	8	2	E	5-15	ND	background (downwind)
4-4	13:15-13:47	9	4	E	3-10	ND	background (downwind)
4-5	13:47-14:19	9	4	ESE	0-10	ND	background (downwind)
4-6	14:19-14:51	9	4	E	0-5	ND	background (downwind)
4-7	14:56-15:28	9	3	E	0-10	ND	MEK only (downwind)
4-8	15:39-16:11	9	3	E	0-10	ND	PCB's (downwind)
4-9	16:11-16:43	9	2	E	0-10	ND	PCB's (downwind)
4-10	17:04-17:36	9	1	E	0-10	ND	PCB's (downwind)
4-11	17:36-18:08	9	0	E	0-10	ND	PCB's (downwind)
4-12	18:47-19:19	10	-1	E	0-10	ND	PCB's (downwind)
4-13	19:19-19:51	10	-1	E	3-15	ND	PCB's (downwind)
4-14	19:56-20:28	10	-1	E	3-15	ND	PCB's (downwind)
4-15	20:28-21:00	10	-1	ENE	0-10	ND	PCB's (downwind)

1: See Figure 1 for sampling locations

2: AT = ambient temperature (^{o}C); WD = (predominant) wind direction; WS = wind speed range in km/hr

3: ½-hour concentration of gaseous PCB's (di- to pentachlorobiphenyls); mean of 15 2-minute samples ND = not detected above detection limit of 0.04 ug/m^3

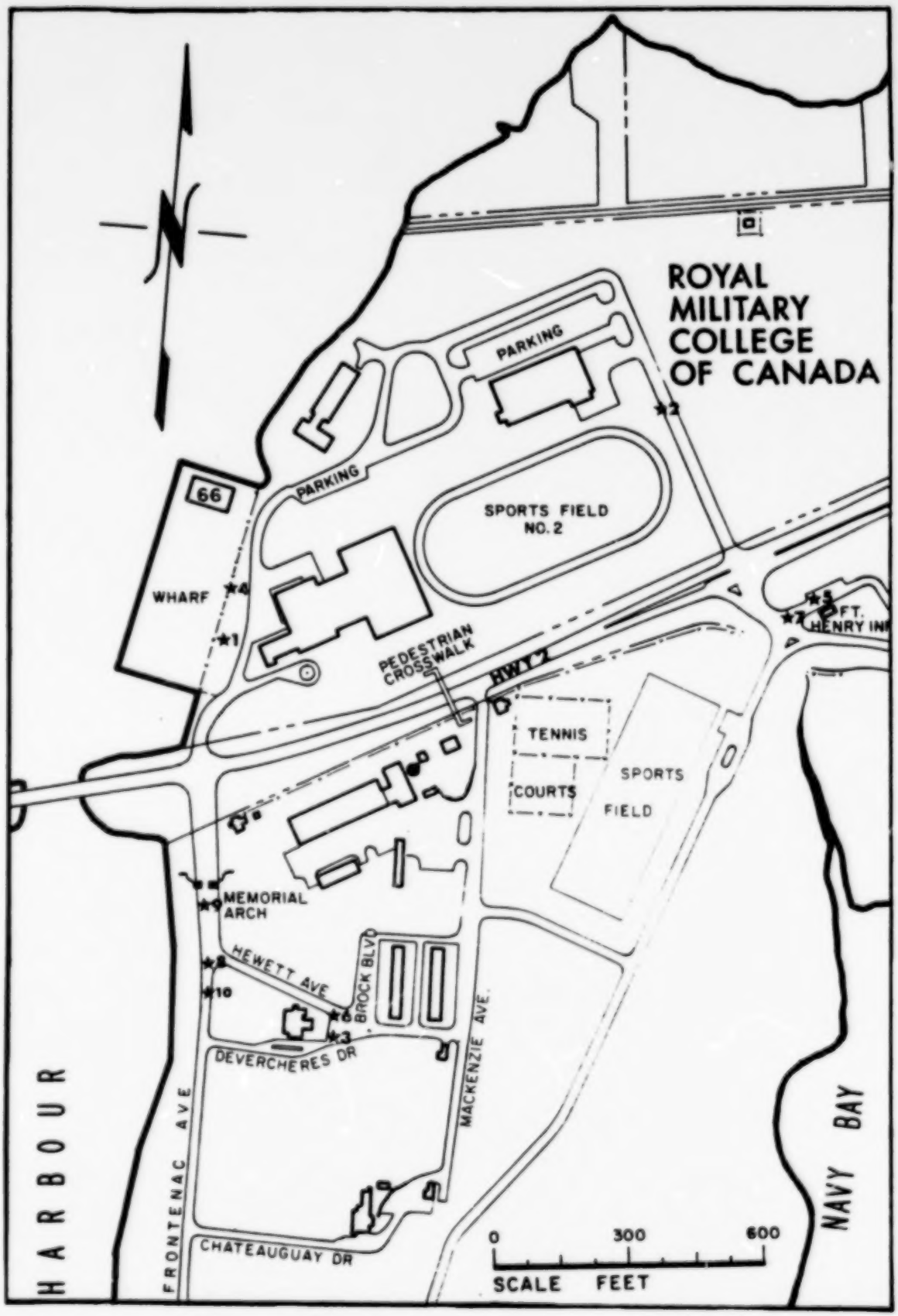


FIGURE 1

● TEST SITE

★ TAGA SAMPLING SITES

APPENDIX A

Air Resources Branch

Mobile TAGA Technology and PCB Monitoring

TAGA TECHNOLOGY

In 1979 the Air Resources Branch of the Ontario Ministry of the Environment acquired a mobile Trace Atmospheric Gas Analyzer (TAGA) from Sciex Incorporated of Thornhill, Ontario. The mobile TAGA unit (MAMU No. 3) has been applied to a variety of air monitoring situations including airborne PCB's. The Ministry has conducted over 50 air quality surveys with the mobile TAGA unit.

The TAGA 3000 is basically a specialized quadrupole mass spectrometer coupled to a unique sample inlet and ion source (See Figure A1). Ionization of pollutants is achieved by chemical ionization initiated by a stable corona discharge operating at atmospheric pressure. Since the ion source permits continuous, direct, air sampling at a high flow rate (100 l/min), it is possible to determine the temporal and spatial distribution of selected pollutant levels. The mobile TAGA's capabilities are especially suitable for plume tracking; that is, tracing a pollutant back to its source of origin.

When equipped with the standard atmospheric-pressure source the TAGA system is sensitive to most volatile compounds containing a heteroatom, such as N, O, S, P and halide. Typical detection limits are in the range of 0.1 to 10 ug/m^3 depending on the type of chemical measured and the sample matrix.

All operations of the TAGA are controlled by a dedicated computer with 28 megabytes of storage. Air quality data are instantly displayed on a CRT unit allowing the operator to assess the data on-site and thus formulate the appropriate survey strategy.

The mobile TAGA unit is also equipped with a 10 metre, telescopic tower and meteorological instrumentation to measure local wind speeds, wind direction and ambient temperature. All meteorological data are stored by the on-board computer simultaneously with the collection of air quality data.

PCB MONITORING METHODOLOGY

For most chemical classes the sensitivity of the TAGA is more than adequate for ambient air monitoring. One exception, however, are the PCB's, where the absolute sensitivity is insufficient for instantaneous real-time detection. Thus in the late 1970s Sciex Inc. developed a simple sampling device to preconcentrate volatile PCB's. Preconcentrating the PCB's for only 2-minutes lowers the detection limits by two orders of magnitude.

Although the basic principles have remained unchanged, today's PCB preconcentrator has evolved into a portable sampling inlet system with all operating parameters under strict computer control. It is commercially known as the Automated Short Term Adsorber or ASTA .

The ASTA, shown in Figure A2, consists of two sample probes formed by coiling a nichrome wire coated with a gas chromatographic stationary phase, OV-17. The positions, and thus function of the two probes, are interchangeable between the adsorption or sampling position, and the desorption or analysis position. While one probe is adsorbing PCB's from the ambient air, the other probe is being desorbed and analyzed for PCB's from a previous air sample. Altering the positions of the two probes permits continuous screening of the ambient air in 2 minute intervals. There is approximately an eight second delay

between sampling periods due to the probe cycling time. Thus a "½-hour sample", which is 15 consecutive 2 minute samples, takes 32 minutes.

When sampling for PCB's the probe is placed directly in the ambient gas stream (1.7 l/s) for a period of 2 minutes. The probe is then changed to the desorb position and 12 volts DC (3.25 amperes) are applied to the probe for a period of 40 seconds. This causes the probe temperature to rapidly increase to approximately 300°C, thereby transferring the PCB's from the OV-17 into the gas phase. The carrier gas, which is a mixture of ultra pure zero air and benzene (100 ppm), constantly sweeps the PCB's into the ion source. Upon entering the ion source the PCB's immediately undergo benzene chemical ionization producing molecular PCB ions (M^+) which are (mass) selectively monitored by the quadrupole mass filter.

The software allows for the screening of 4 PCB congeners at 8 masses, 2 isotopes per congener. Normally the dichlorobiphenyl to pentachlorobiphenyl species are monitored. There are two reasons for this: firstly, the TAGA is more sensitive to these species, and secondly; PCB's with lower molecular weights generally exhibit higher vapour pressure, thus increasing the likelihood of gas phase detection.

Calibration of the system, including sampling probe adsorption efficiencies and TAGA response, is accomplished by continuously injecting known amounts of PCB's directly into the air sampling steam via a heated injection port (300°C) using a gas-tight syringe and motorized syringe drive. The PCB standards are prepared by the dissolution of pure PCB isomers, one per congener, into iso-octane. Repeated injections at 5 different syringe drive settings establishes a calibration curve which is linear (correlation coefficients are

usually better than 0.995) over the PCB concentration range of 0.425 to 2.5 ug/m^3 per congener. The relative standard deviations for multiple injections of PCB standards are typically better than 5% at the 0.425 ug/m^3 level.

DATA PROCESSING AND INTERPRETATION

Immediately following a desorption of the probe, the TAGA computer calculates the level of PCB's (or equivalents) per congener, per isotope, from the net signal (sample minus background) and the daily calibration factors. In fact, for each PCB congener group, two measurements are made: one for the chlorine 35 isotope (M); and one for the corresponding chlorine 37 isotope (M+2).

At this stage the field survey scientist interprets the reduced data using the following criteria:

1) the desorption peak (integrated signal) must be at least 3 times greater than the probe noise (S/N>3);
2) the PCB levels for a given isotope pair must be within the overall experimental accuracy of 20%;
3) the calculated isotope ratios must be within 10% of the theoretical isotope ratio for a given congener.

If condition 1) above is not satisfied, the congener concentration will be below the detection limit and a ND is reported. If conditions 2) and 3) are not evident then a chemical interference at one, or both, of the congener mass(es) is assumed to present, and the lower concentration value of the two isotopes is assigned the upper concentration limit for that particular PCB congener.

The PCB detection limits for the TAGA/ASTA technique is defined as being 3 times the standard deviation of the background signal observed at the

PCB masses, divided by the appropriate calibration factors. Thus by definition, the detection limits depends on two important factors:

i) the sensitivity, which is a function of the probe adsorption efficiencies and the benzene chemical ionization rates.

ii) the level of the interferences (absorbed compounds that have the same nominal ionic mass as the targetted PCB's in both upwind and downwind air samples). Interference levels are highly variable depending on the sampling site, the source(s) in the immediate area, and the local meteorological conditions.

During a survey air samples are spiked periodically with 0.425 ug/m^3 per PCB congener to establish the daily sensitivity factors and determine, on-site, the detection limits of the technique. Typical detection limits range from 0.01 to 0.05 ug/m^3 per congener, or from 0.04 to 0.20 ug/m^3 for total (di to pentachlorobiphenyls) PCB's, depending on the complexity of the sample matrix.

SUMMARY

The TAGA/ASTA PCB monitoring technique is a specialized application of the mobile TAGA 3000. It was developed to rapidly screen the ambient air for volatile PCB's. Important features of the technique to consider when assessing the data are:

1) The technique measures gas phase PCB's, not those associated with particulates or existing as aerosols.

2) PCB's levels are determined continuously every 2 minutes.

3) Four congeners are monitored simultaneously (normally the dichlorobiphenyls to pentachlorobiphenyls).

4) The detection limits for total PCB's typically range from 0.04 to 0.20 ug/m^3 depending on the sample matrix.

TAGA 3000 SYSTEM

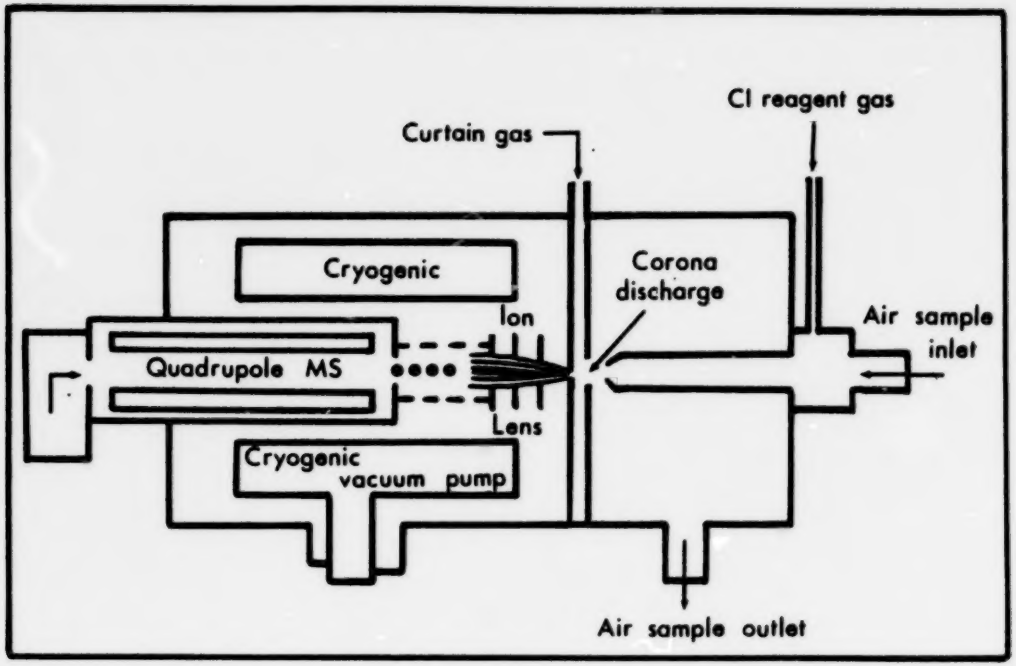


Figure A1: Schematic of the TAGA 3000.

ASTA SCHEMATIC

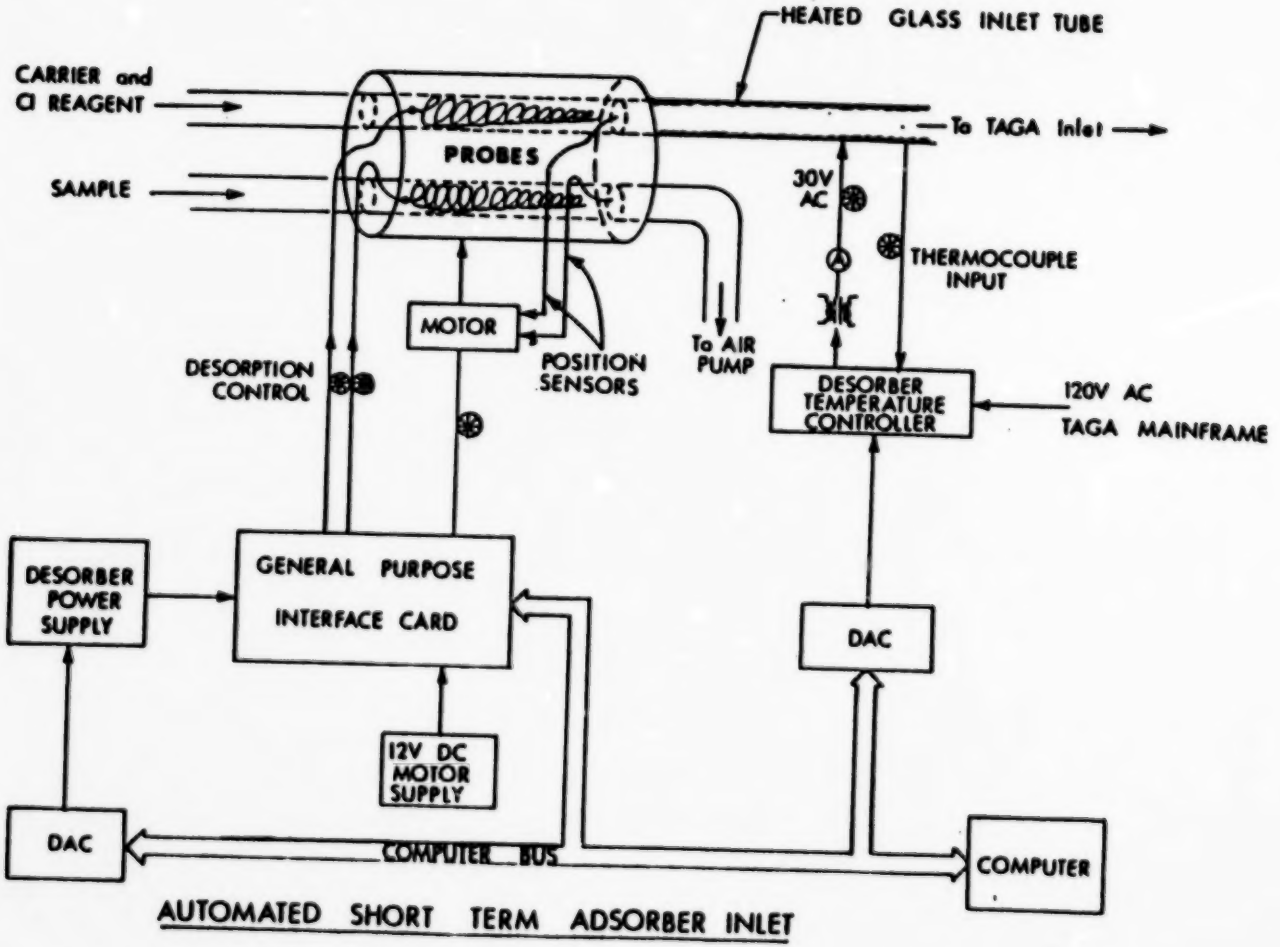
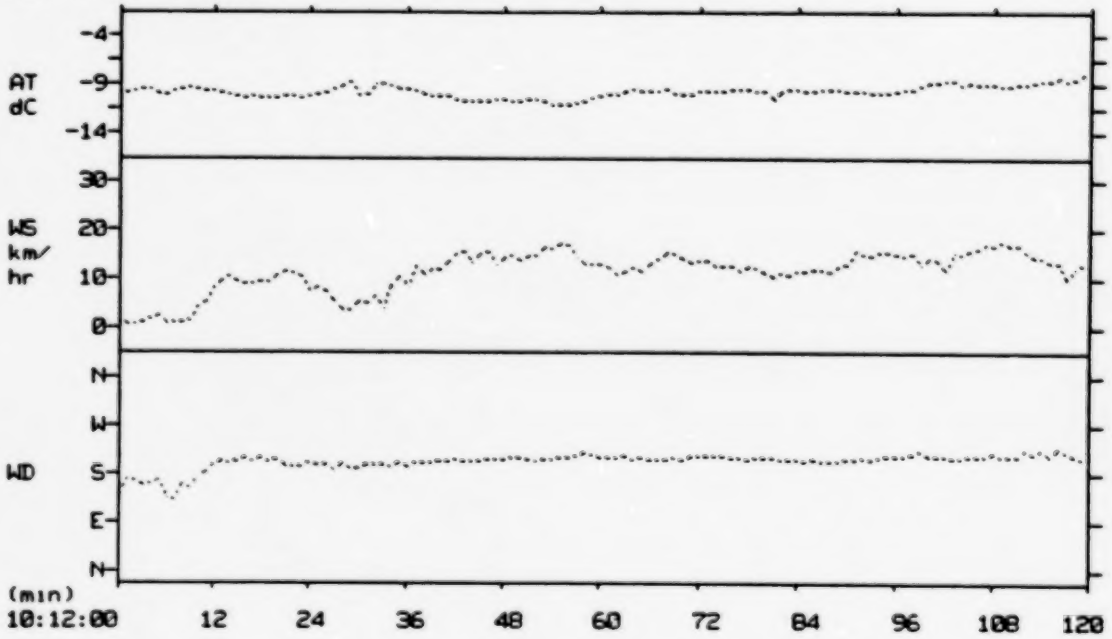


Figure A2: Schematic of the ASTA used in conjunction with the TAGA PCB Monitoring technique.

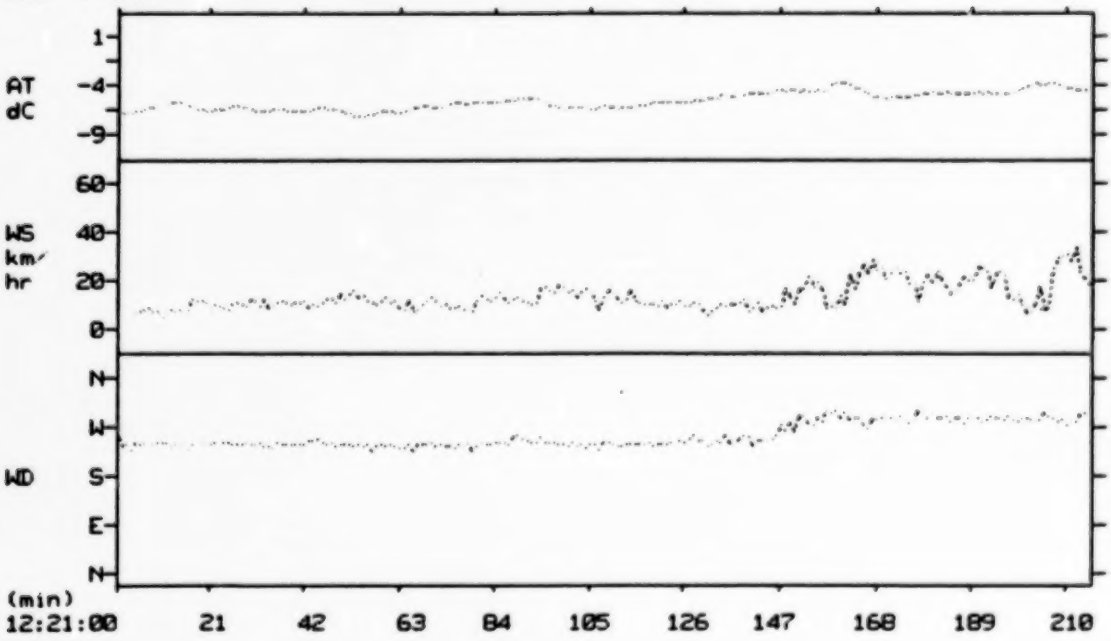
APPENDIX B

Meteorological Data
Mobile TAGA Station
RMC, Kingston PCB Survey (1986)

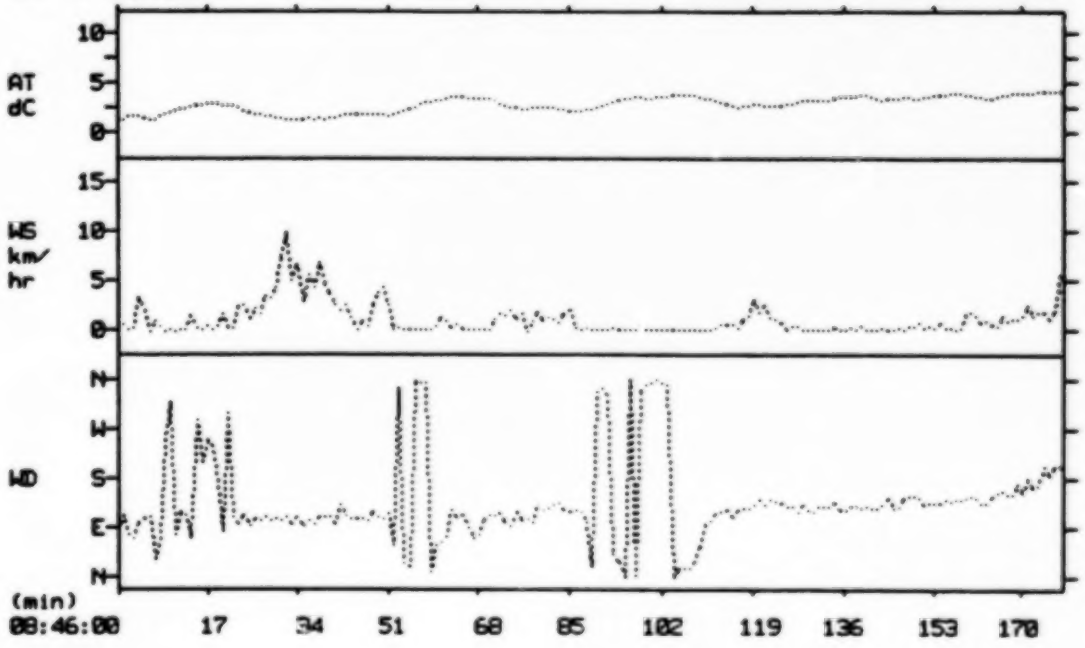
Start: 86/02/12 10:11:00 File: KI1201.MET
Scan : 30 sec Ave: 1.00 min Rep: 1.00 min Rnd: 1.0 min
Loc : SARGENTS MESS N OF #2
Met : SUNNY & COLD



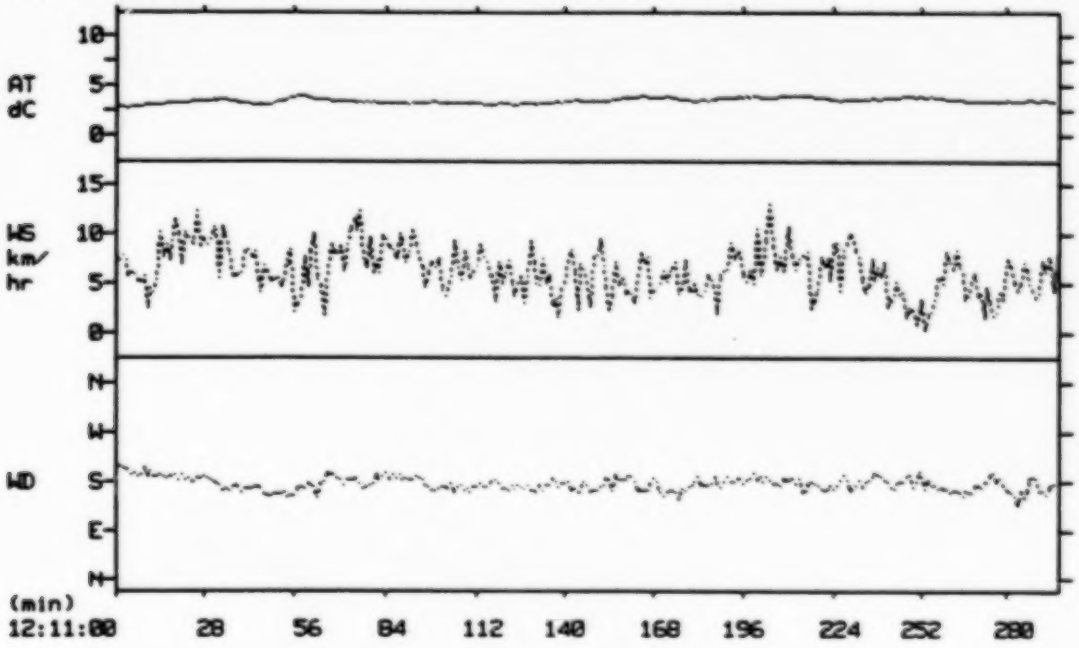
Start: 86/02/12 12:20:30 File: KI1204.MET
Scan : 30 sec Ave: 1.00 min Rep: 1.00 min Rnd: 1.0 min
Loc : EAST OF SPORTS FIELD NO.2
Met : SUNNY



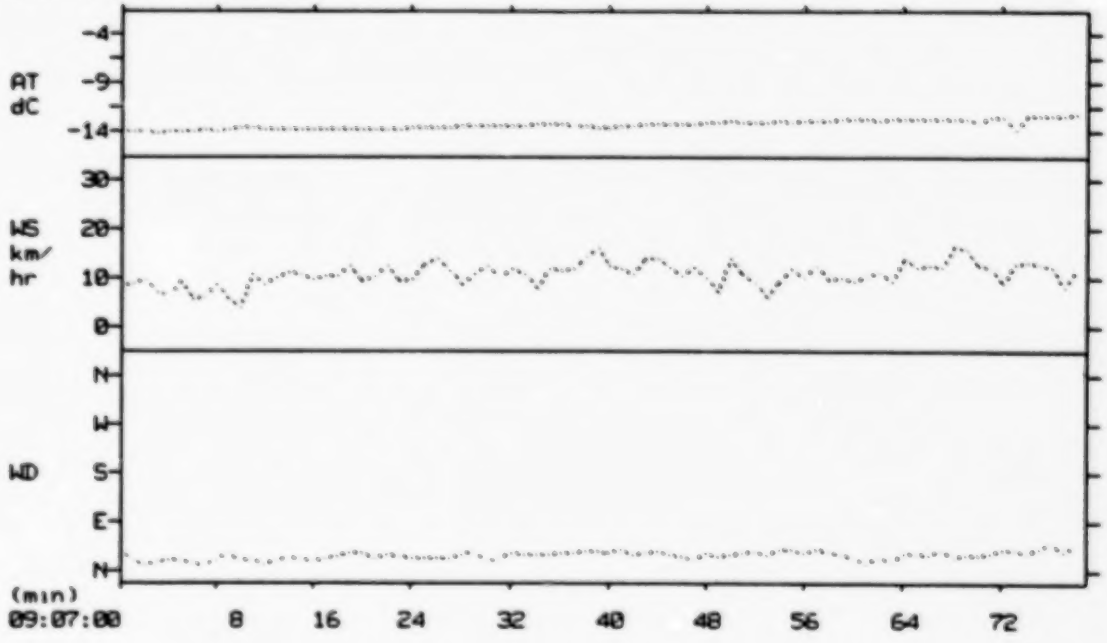
Start: 86/02/20 08:45:30 File: KI2001.MET
Scan : 30 sec Ave: 1.00 min Rep: 1.00 min Rnd: 1.0 min
Loc : SITE HEWETT AVE. & BROCK BLVD.
Met : OVERCAST



Start: 86/02/20 12:10:30 File: KI2004.MET
Scan : 30 sec Ave: 1.00 min Rep: 1.00 min Rnd: 1.0 min
Loc : BETWEEN WHARF & SARGENTS MESS
Met : OVERCAST

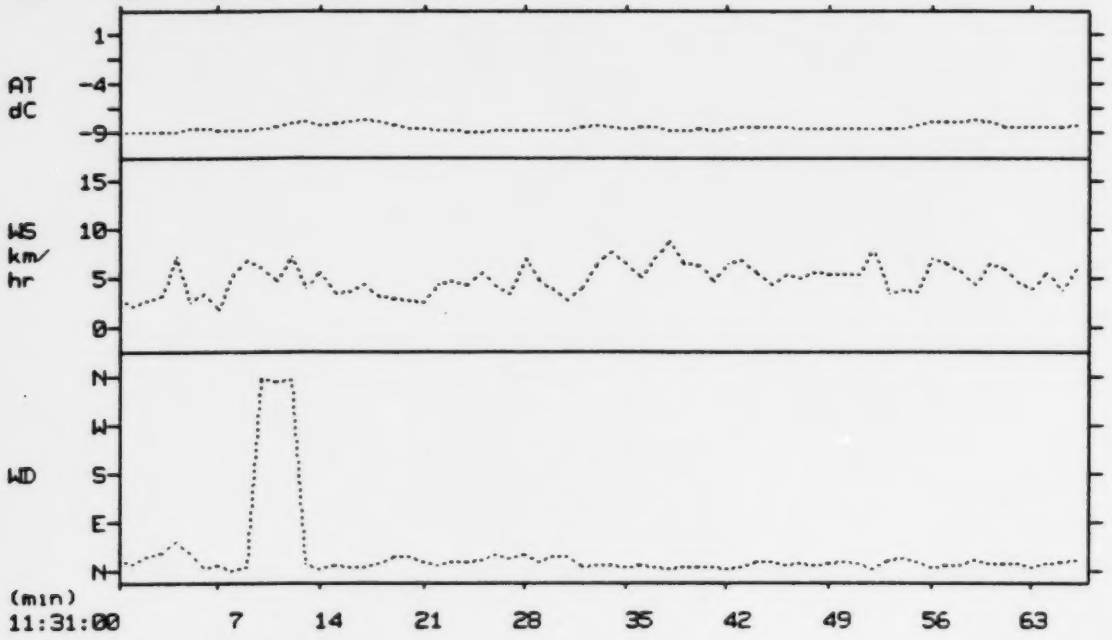


Start: 86/02/22 09:06:00 File: KI2201.MET
Scan : 30 sec Ave: 1.00 min Rep: 1.00 min Rnd: 1.0 min
Loc : INFO CENTRE HWY 2
Met : SUNNY CLEAR COLD

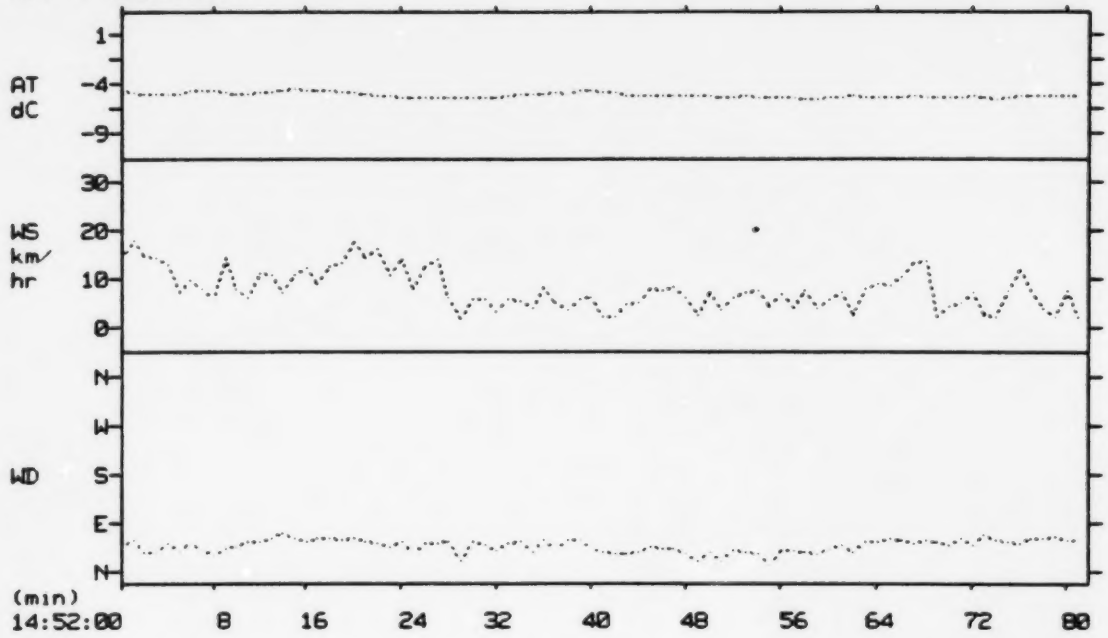


(min)
09:07:00 8 16 24 32 40 48 56 64 72

Start: 86/02/22 11:30:30 File: KI2202.MET
Scan : 30 sec Ave: 1.00 min Rep: 1.00 min Rnd: 1.0 min
Loc : HEWLETT / BROCK
Met : SUNNY COLD NE WINDS CLEAR



Start: 86/02/22 14:51:00 File: KI2203.MET
Scan : 30 sec Ave: 1.00 min Rep: 1.00 min Rnd: 1.0 min
Loc : HEWLETT & BROCK
Met : CLEAR SUNNY



Start: 86/03/12 09:18:30 File: KI1201.MET
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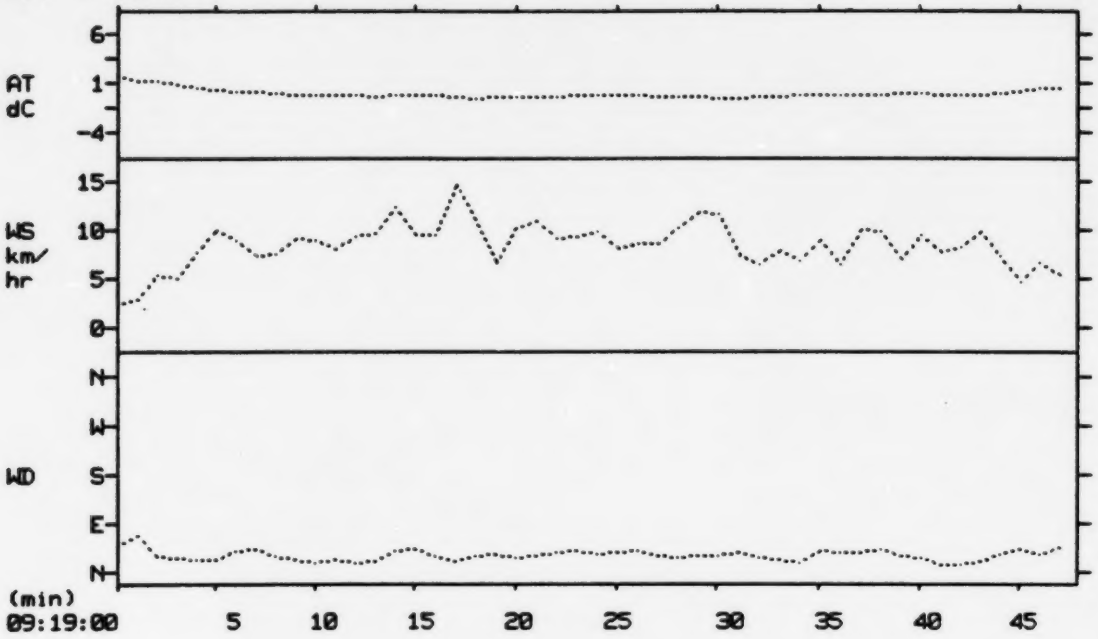
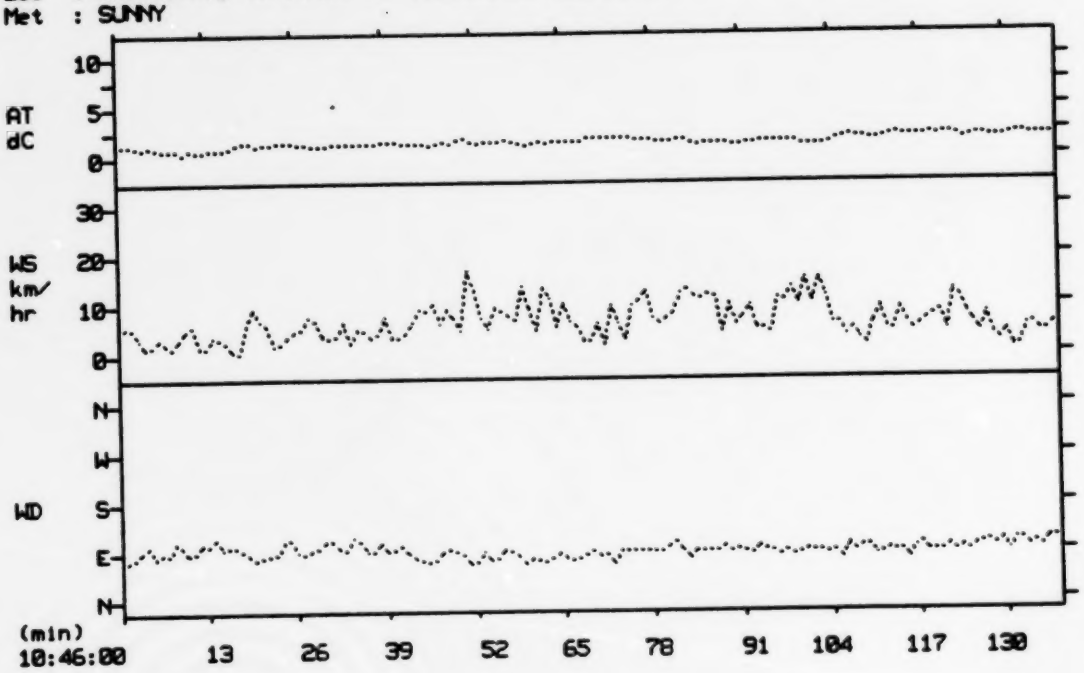
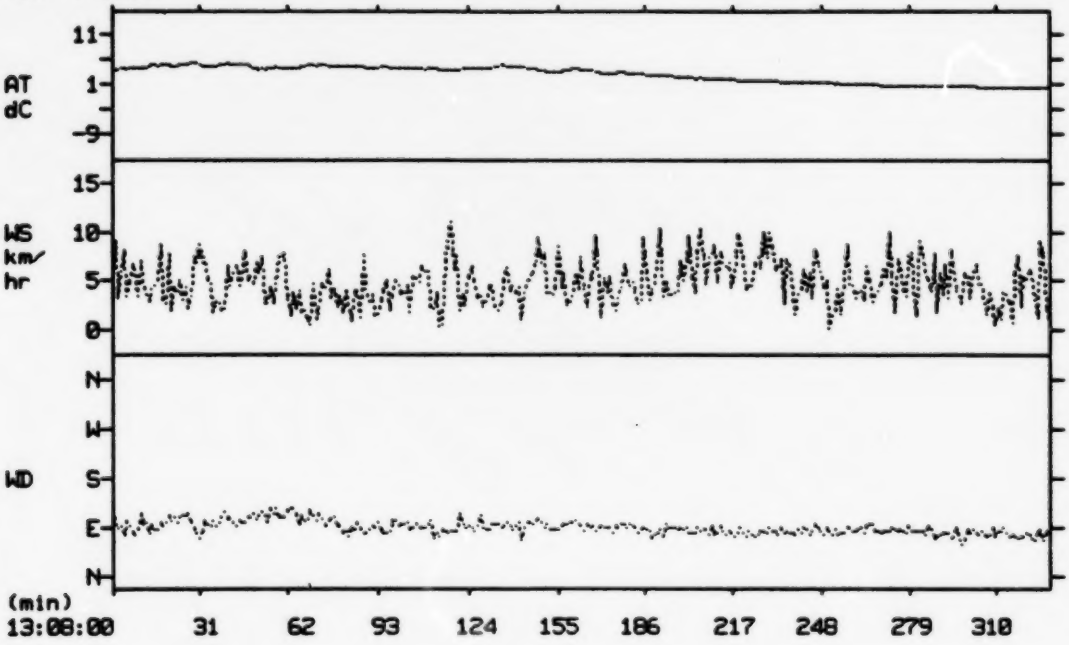
Loc : INFO CENTRE
Met : SUNNY



Start: 86/03/12 10:45:30 File: KI1202.MET
Scan : 30 sec Ave: 1.00 min Rep: 1.00 min Rnd: 1.0 min
Loc : FRONTENAC; IN FRONT OF PRINCIPAL RESIDENCE
Met : SUNNY



Start: 86/03/12 13:07:00 File: KI1204.MET;2
Scan : 30 sec Ave: 1.00 min Rep: 1.00 min Rnd: 1.0 min
Loc : FRONTENAC: SOUTH OF ARCH, NORTH OF HEWETT
Met : SUNNY



Start: 86/03/12 18:42:30 File: KI1209
Scan : 30 sec Ave: 1.00 min Rep: 1.00 min Rnd: 1.0 min
Loc : FRONTENAC; IN FRONT OF PRINCIPAL RESIDENCE
Met : CLOUDY